CHAPTER 4

Phase behavior of linear-comb copolymer in WSL

4.1 Introduction

In this chapter the stability analysis of chapter 2 is extended. The microphase separated morphologies of a melt of a specific class of linear-comb block copolymers, A_m-*b*-(A-*g*-B)$_n$, is analyzed in the weak segregation limit. On increasing the length of the linear A-block, the systems go through a characteristic series of structural transitions. Starting from the pure comb copolymer the first series of structures involve a short length scale followed by structures involving a large length scale.

Diblock copolymer melts usually microphase separate with *one* characteristic length. However, if more than two monomer types are involved microphase separation frequently occurs at more than one length scale. [3–5, 53–55, 59] Several examples, that are of direct interest for the present chapter, can be found in the experimental work of Ikkala and Ten Brinke. [3–5] Linear-comb copolymers are investigated consisting of a poly(4-vinyl pyridine)-*block*-polystyrene (P4VP-*b*-PS) diblock copolymer with side chains (e.g. pentadecylphenol, PDP) attached by hydrogen bonds to the P4VP-block. The resulting linear-comb copolymers show typical two length scale structure-*inside*-structure morphologies. The PS-blocks microphase separate from the P4VP(PDP)-blocks giving rise to the well known classical morphologies depending on the volume fraction of either block. This structure corresponds to the large length scale ordering and the order-disorder transition tempera-

ture is, if present at all, very high. Inside the P4VP(PDP) domains an additional short length scale lamellar ordering takes place characterized by an easily accessible (ca. 60^oC) order-disorder transition. See also the discussion in the introductory chapter.

Still, two length scale ordering is not restricted to block copolymers involving three or more chemically different monomers. As was demonstrate in a forgoing chapter where we studied the structure factor of a specific class of linear-comb and linear-alternating block copolymers melt. (An experimental example can be found in Refs. [103–106]) In this chapter we will only consider linear-comb block copolymers.

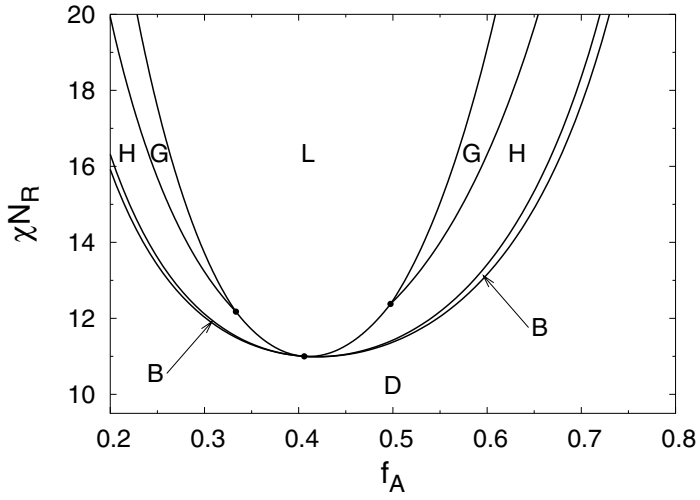
For convenience, to reduce the number of free parameters, the discussion was restricted to side chains having a length equal to the backbone length between two consecutive side chains, see figure 2.6. Due to the architecture of the molecule microphase separation can in principle occur at two different length scales, either 'inside' the AB-comb block or 'between' the linear A-block and the AB-comb block, see figure 2.2. In the latter case the behavior resembles that of a diblock copolymer, where one block is the linear A-block and the other block the AB-comb block.

In chapter 2 the analysis of the structure factor of this system was presented and the main result was summarized in the form of a so-called classification diagram. Here, we continue the analysis of the phase behavior of this class of systems by calculating the free energy up to fourth order in the weak segregation limit and constructing the corresponding phase diagrams.

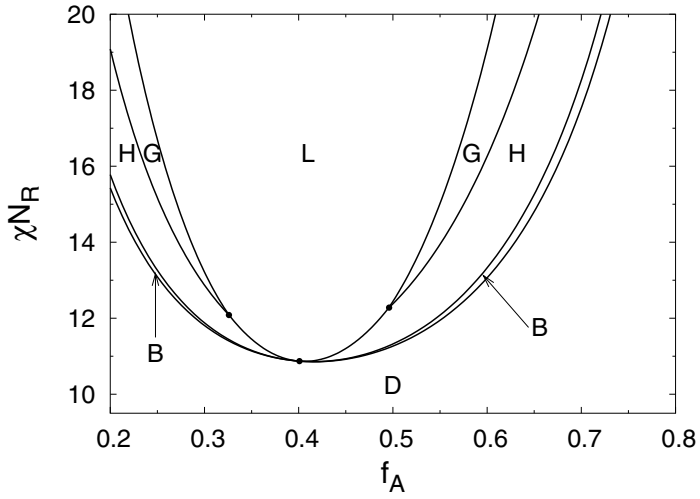
4.2 Phase behavior of comb block copolymer

Before we consider the linear-comb copolymers, we start with some phase diagrams pertaining to pure comb copolymer melts only. For two different comb copolymers, corresponding to $(n, \alpha, t) = (10, 1, \frac{1}{2})$ and $(30, 1, \frac{1}{2})$, these are plotted in figures 4.1(a) and 4.1(b). The lines delineate the boundaries between the regions where the different structures are stable. The phase boundaries are asymmetric and elevated compared to a diblock copolymer melt.

Altogether, the phase diagrams show the 'normal' shape and morphologies as expected from the literature on melts of complex block copolymers. [74, 86, 97–99] The asymmetry is obvious due to the fact that the architecture of a comb copolymer is not invariant under the interchange of A- with B-monomers or f with $1 - f$. The elevation of the phase boundaries agrees with the general observation that in more complex polymer melts the disordered phase is more stable, meaning that the ODT



(a)



(b)

Figure 4.1: Phase diagram corresponding a comb block copolymer melt with (a) $n = 10$ side chains and (b) $n = 30$ side chains, for both correspond to $(\alpha, t) = (1, \frac{1}{2})$, i.e. one side chain per branch point which grafted symmetrically with respect to both ends of the backbone. Note that $N_R = N/n$ corresponds to the number of monomers of *one* repeat unit.

shifts to lower temperatures as compared to the ODT of a diblock copolymer melt. [61, 99, 107] This is due to the fact that more complex block copolymer melts 'loose' relatively more entropy on structure formation. [107, 108]

The increase of the number of side chains from $n = 10$ to $n = 30$ has only a relative small effect on the location of the phase boundaries. Thus, increasing the number of repeat units, i.e. n, does not affect the general phase behavior of comb copolymers. This is in line with the observation of chapter 2 that the phase behavior primarily is controlled by the size one repeat unit.

4.3 Phase behavior of linear-comb block copolymer

We start the discussion concerning the phase behavior of linear-comb block copolymer melts by presenting first the critical points after which a number of phase diagrams are shown and discussed.

4.3.1 Critical points of linear-comb copolymers

We consider the specific class of linear-comb copolymers, characterized by side chains of a length equal to the length of the backbone between consecutive side chains. Therefore, an increase in f_A corresponds to an increase in the length of the linear polymer A-block ($N_A^l = md$).

Because of this, critical points will only be found for special values of n and m (f_A). In figure 4.2 these critical points are presented by the dashed and dotted line. The curve has two branches, an upper and a lower branch. The upper branch is associated with the large length scale structure, i.e., the diblock scale separation. The lower branch corresponds to the short length scale, i.e. separation within the comb block. The part of the lower branch located inside region Ls, indicated by the crosses, does not correspond to true critical points anymore. They are a "pseudo" critical points. In region Ls the absolute minimum of Γ_2 corresponds to the large length scale. The critical points are associated with the relative minimum of Γ_2. For the position of the absolute minimum of Γ_2, Γ_3 does not become zero. The "pseudo" critical point is defined accordingly

$$\left.\frac{\partial\gamma_2(q)}{\partial q}\right|_{q=q_{min}} = 0 \quad \left.\frac{\partial^2\gamma_2(q)}{\partial q^2}\right|_{q=q_{min}} > 0 \quad q_{min} \neq q^* \quad \wedge \quad \gamma_3(\mathbf{q},\mathbf{q}',\mathbf{q}'') = 0 \quad \wedge$$
$$\|\mathbf{q}\| = \|\mathbf{q}'\| = \|\mathbf{q}''\| = q_{min}. \quad (4.1)$$

Contrast this expression which the definition of the true critical point of equation 3.138.

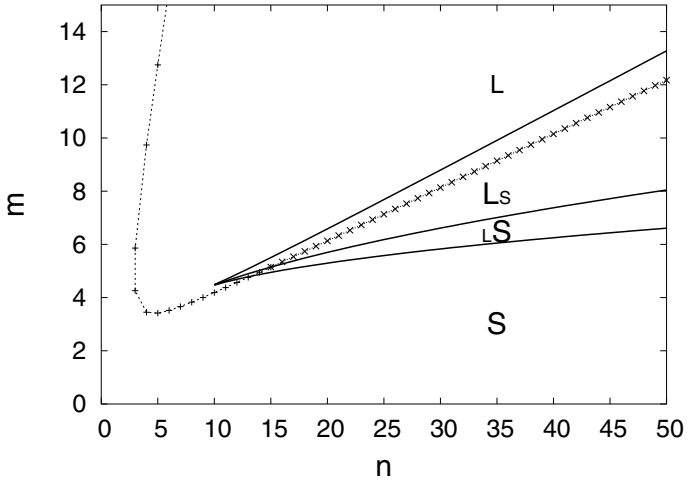


Figure 4.2: Critical points for linear-comb copolymers melts defined in the text. The classification diagram of the class of linear-comb is also shown. The pluses (+) and crosses (×) indicated the critical points and the "pseudo" critical points respectively.

For n-values ranging from 3 to 15, critical points are present for two values of m. For $n > 15$, the critical point corresponding to the short length scale ordering no longer corresponds to the absolute minimum of $\Gamma_2(q)$. In contrast, for $n = 2$ there is no critical point at all. Of course, this is simply due to the specific choice of parameters. We selected $N_B = N_A^b/n = d$, $\alpha = 1$ and $t = 0$ and for $n = 2$ the critical point is located outside this particular subset of parameters.

In figure 4.3, the critical points of the linear-comb copolymer melt are presented once more. This time in the (n, f_A) plane. This presentation is better suited to show the upper branch corresponding to the critical points of the large length scale structure formation. It clearly illustrates the presence of two critical points (two values of m) for $n > 2$. Of course, for $n > 15$, the lower branch corresponds again to "pseudo"critical points.

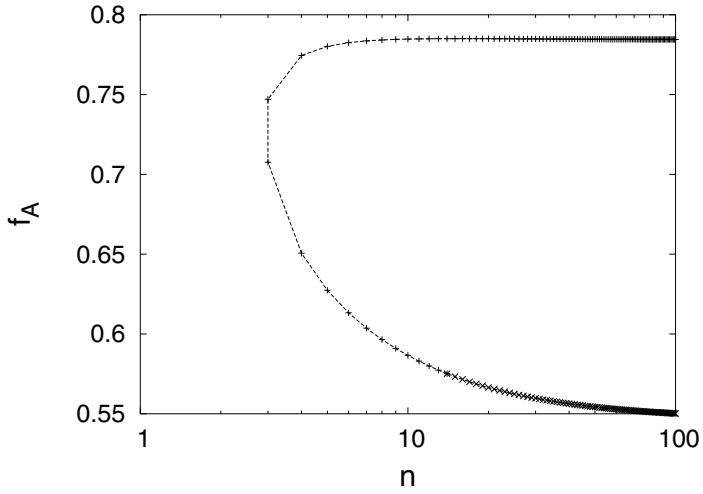


Figure 4.3: Critical points for linear-comb copolymers. The part of its lower branch indicated with crosses ($n > 15$) denote the "critical points" located in region Ls.

4.3.2 Selected phase diagrams

As became clear from the spinodal analysis, the phase behavior of linear-comb copolymers will be much richer. One way of presenting a phase diagram for this class of systems is to fix n and vary m or equivalently vary f_l. In this way we start with a pure comb copolymer for $m = 0$ and end with nearly pure linear polymer for $m \gg 1$. However, the existence of a bifurcation point in parameter space separating two distinct regions complicates matters. If we start with $n > 10$, the second order vertex function will develop two minima on increasing m. First the absolute minimum corresponds to the short length scale ordering. On increasing m two minima appear and for a specific value of m the minima attain the same value. On increasing the length of the linear block further the absolute minimum corresponds to the large length scale and, finally, the minimum belonging to the short length scale gradually disappears. (See the spinodal curve of chapter 2, figure 2.8.) As presented in theory section of the previous chapter, the analysis of the stability of various ordered structures in block copolymer melts is usually based on a free energy expansion using a single dominant wave vector q^*, where q^* coincides with the q-value for which the second order vertex function attains its minimum. So, it is quite obvious that the analysis of the

microphase separated morphology in the case where the second order vertex function has two minima of nearly equal value requires a completely different analysis involving the q-values of both minima. (See Ref. [109].) Here we will restrict ourselves to the region in the classification diagram left of the bifurcation point where there is always only one minimum and the theory (WSL) outlined before can be applied without any restriction.

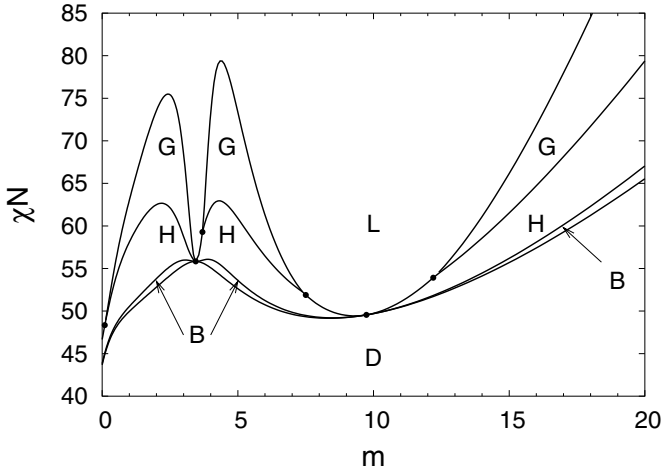
The phase diagrams that are presented, correspond to a fixed number of branch points (n) and varying length of the linear A-block (m or f_l), i.e. to slices in the (n, m) or (n, f_l) plane for fixed n. Figures 4.6 and 4.5 correspond to $n = 2$ and $n = 4$ respectively. These phase diagrams are presented as χN versus f_l. However, phase diagram 4.4(a) is presented as χN versus m.

For $n = 4$ the phase diagram has two critical points. The critical point on the left signals the change from ordering on the short (comb) length scale to ordering on the long (diblock) length scale. The critical point on the right corresponds to the critical point of the effective diblock copolymer. The difference in nature of both critical points is clearly illustrated in figure 4.4(b), presenting the phase diagram around the left critical point. The different behavior around the two critical points has to attributed to the difference in properties of γ_3. For a symmetric diblock $\gamma_3 = 0$ for any q-vector, this corresponds to the situation at the right critical point, this is ,however,not the case of around the left critical point. There γ_3 is only zero for certain values of the q-vector.

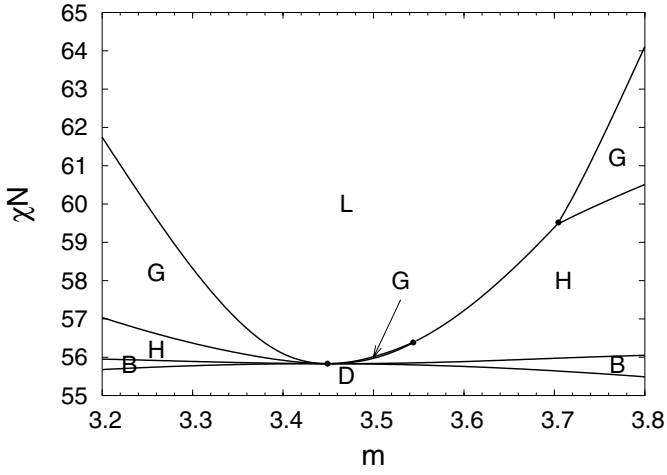
Throughout the phase diagram the lamellar (resp. hexagonal, gyroid and spherical) structure is indicated with the same character L (resp. H, G and B). It should be realized, however, that the same symmetry is accompanied with strongly different periodicities in different regions of the phase diagram. Therefore we have plotted the phase diagram 4.5(a) once more, now accompanied with the domain spacing 4.5(b), which illustrates the change of length scale and structure on changing the length of the linear A-block, i.e. f_l or m.

To illustrate this we will walk through the phase diagram, figure 4.5(a), as a function of the length f_l of the linear polymer block keeping the value of χN fixed at 60, respectively 55. The corresponding changes in length scale can be found from figure 4.5(b).

Let us start with $\chi N = 60$. For f_l sufficiently small there is a short length scale lamellar ordering, the layers being alternately rich in side chain B-monomers and A-monomers. Then a short length scale hexagonal structure is found with cylinders rich in side chain B-monomers. Then a kind of in between "intermediate"length scale

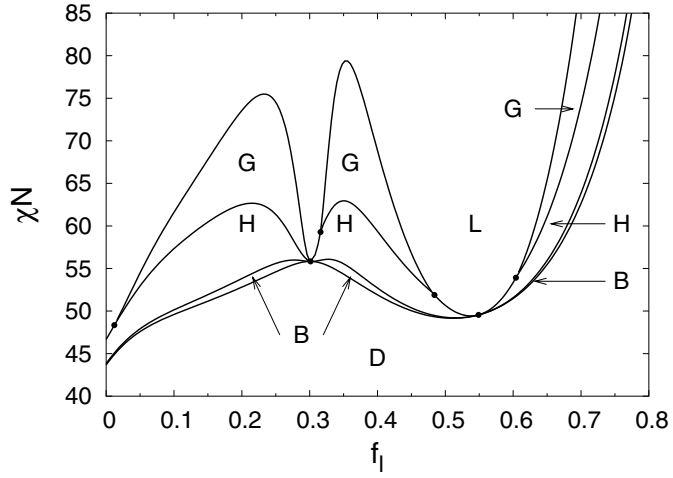


(a) Phase diagram

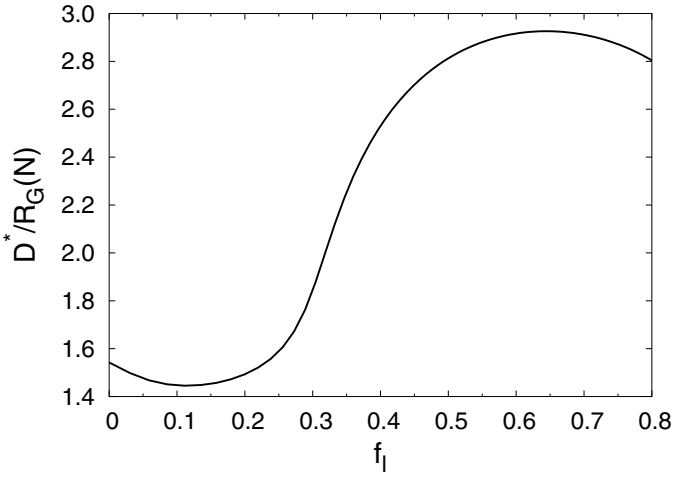


(b) Phase diagram; zoomed in around left critical point

Figure 4.4: (a) Phase diagram for the class of linear-comb copolymer melts defined in the text. The figure corresponds to molecules with a comb-block characterized by four branch points $n = 4$, asymmetry parameter $t = 0$, and one side chain per branch point $\alpha = 1$. Note that m corresponds to the length of the linear A-block.(A_m-b-(A-g-B)$_4$). D = disordered, L = lamellar($\bar{1}$), H = hexagonal ($p6mm$), B = spherical ($Im\bar{3}m$), and G = gyroid ($Ia\bar{3}d$). (b) Zoomed in around left critical point.

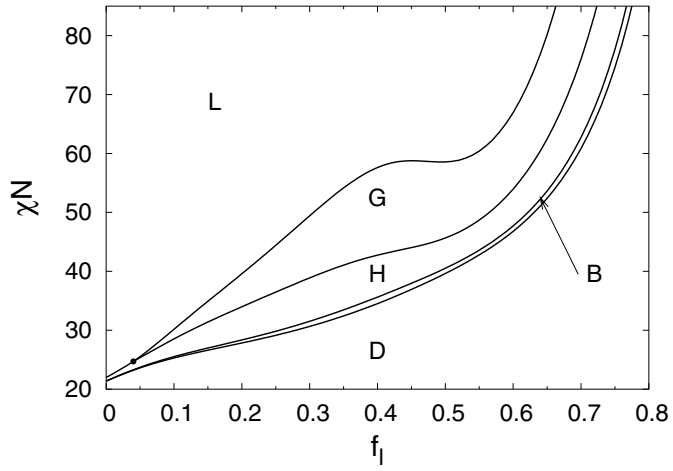


(a) Phase diagram

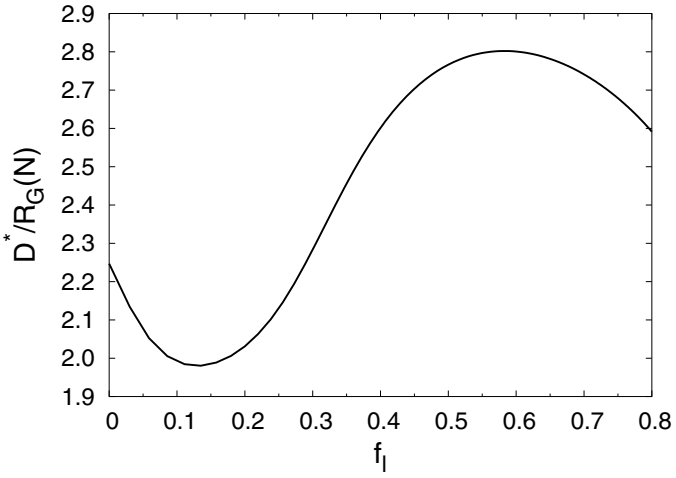


(b) Domain spacing

Figure 4.5: (a) Phase diagram and (b) domain spacing for linear-comb copolymer melts characterized by four branch points $n = 4$, asymmetry parameter $t = 0$, and one side chain per branch point $\alpha = 1$. f_l corresponds to the volume fraction of the linear A-block. (A_m-*b*-(A-*g*-$B)_4$). D = disordered, L = lamellar($\bar{1}$), H = hexagonal (*p*6*mm*), B = spherical ($Im\bar{3}m$), and G = gyroid ($Ia\bar{3}d$).



(a) Phase diagram



(b) Domain spacing

Figure 4.6: (a) Phase diagram and (b) domain spacing for linear-comb copolymer melts characterized by two branch points $n = 2$, asymmetry parameter $t = 0$, and one side chain per branch point $\alpha = 1$. f_l corresponds to the length of the linear polymer A-block. (A_m-b-(A-g-$B)_2$). D = disordered, L = lamellar($\bar{1}$), H = hexagonal ($p6mm$), B = spherical ($Im\bar{3}m$), and G = gyroid ($Ia\bar{3}d$).

lamellar structure is formed, followed by a large length scale hexagonal structure with cylinders rich in linear polymer A-monomers. Next, the sequence of structures follows the usual pattern from lamellar (layers alternately rich in linear polymer block and comb copolymer block) to hexagonal (cylinders rich in comb copolymer block) to bcc (spheres rich in comb copolymer block) to disordered.

For $\chi N = 55$, we start again with a short length scale lamellar structure (layers alternately rich in side chain B-monomers and A- monomers) followed with a short length scale hexagonal structure (cylinders rich in side chain B-monomers). A sequence of short length scale bcc (spheres rich in B-monomers), disordered state and large length scale bcc (spheres rich in comb copolymer block) is then found. Next, the structures follow the same order as discussed above for $\chi N = 60$.

In above discussion we have omitted the gyroid structure in order to avoid further complicating the sketched behavior. However, it should be emphasized that in both examples one traverse, when going for a lamellar to a hexagonal phase, also through a gyroid structure. Note also that within a strictly first harmonic analysis the gyroid structure is absent, see Ref [110].

For $n = 2$ the phase diagram does not have any critical point. As discussed before, this is simply due to the choice of parameters. Going through the phase diagram at constant value of χN, e.g. 40, there is a much more gradual change in length scale.

4.3.3 Second-harmonic approximation and two length scale problem

In this section, we consider briefly the extension of the second harmonic approximation to the two length scale problem. Following section 3.5.4, one might propose the following generic free energy,

$$F = \gamma_2(q_s)S^2 + \gamma_2(q_l)L^2 + \gamma_3(q_s, q_s, q_l)S^2L + \gamma_3(q_s, q_s, q_s)S^3 + \gamma_3(q_l, q_l, q_l)L^3 + \gamma_4(q_s, q_s, q_s, q_s)S^4 + \gamma_4(q_l, q_l, q_l, q_l)L^4 + \cdots \quad (4.2)$$

Here S is the amplitude corresponding to the short length scale q_s and L the amplitude belonging to the long length scale q_l. For simplicity any prefactors have omitted been

In section 3.5.4, we argued that higher harmonic contributions to the free energy could be safely ignored as long as $\gamma_2(q_i) > 0$, where i labels the higher order harmonics. Consequently, we are restricted to those polymer systems, i.e. values of n and m, for which $\gamma_2(q_s) \simeq \gamma_2(q_l)$ and thus to those regions in the bifurcation diagram where both scattering peaks have the same value (situation E) or almost the same value; see figure 2.7(c).

If e.g. $\gamma_2(q_l) \ll \gamma_2(q_s)$ then higher order harmonics belonging to the long length scale q_l become important before the short length scale contribution to the free energy seriously effects the balance in free energy. Clearly, considering a large number of harmonics is outside the scoop of weak-segregation theory. $\gamma_2(q_l) \ll \gamma_2(q_s)$ means that there is a large temperature gap between the 'spinodals' of the long and the short wave instability. Thus, the long length scale structure is expected to be already well developed before the short wave instability occurs. Lowering of the temperature leads in general to a more developed structure in block copolymer melts: the different domains become purer and the interfaces become sharper. However, this can not appropriately be described within weak segregation theory and we have to consider different theories to describe the behavior of block copolymer melts at temperatures far away from the ODT.

So, we are left which the situation where both wave instabilities, i.e. q_s and q_l, have equal or almost equal spinodal temperature. From the above free energy expression we gather the following. If $\gamma_2(q_l) \lesssim \gamma_2(q_s)$, $\gamma_2(q_l) < 0$ and $\gamma_2(q_s) > 0$ then the long length scale structure associated with amplitude L may induce a short length scale structure. S can become non-zero because the third order term $\gamma_3 S^2 L$ can become negative and hence lower the free energy. The reverse, a short length scale structure inducing a long length structure, is clearly impossible because a term $L^2 S$ generally does not exit, since $\mathbf{q}_l + \mathbf{k}_l + \mathbf{q}_s \neq 0$ when $q_s > 2\mathbf{q}_l$. Here $\mathbf{q}_l$ and $\mathbf{k}_l$ are vectors of length q_l whereas $\mathbf{q}_s$ is a vector of length q_s. The size of the amplitudes, determining the range of validity of the approximation, depends on the strength of the coupling between the long and short length scale, i.e. terms like $\gamma_3 S^2 L$.

We considered the following structures which have intrinsically two length scales: a rectangular lattice ($p2mm$), a centered rectangular lattice $c2mm$ and a perforated hexagonal structure ($R\bar{3}m$). Depending on the size of the amplitudes S and L the centered rectangular structure 'looks' either like a modulated lamellar or like a deformed hexagonal structure (a hexagonal structure which has been flattened in one direction).[111]

The free energies are analyzed for the case $(n, m) = (15, 5.0240)$, where both wave instabilities appear simultaneously ($\gamma_2(q_s) = \gamma_2(q_l)$). A stable $c2mm$ and $p6mm$ was found. However, their amplitudes were very large: $\|\psi\| \not\ll 1$. Clearly, higher order harmonics corrections are needed. The coupling between both amplitudes is particular strong and consequently the amplitudes become equally large. This is obviously due to the absence of any critical point; see figure 4.2. In the vicinity of a critical point the contribution of γ_3 to the free energy is suppressed and the ampli-

tudes are prevented from becoming large. Only then is at the ODT the phase transition weakly first order. Hence, the weak segregation formalism, as presented in the previous chapter, is inapplicable within regions of the classification diagram where two wave instabilities appear in the scattering function.

4.4 Conclusion

Phase diagram 4.5 seems quite characteristic for the class of linear-comb copolymers considered. For sufficiently large values of χN a sequence of structures is found as a function of the linear polymer A-block length m. The first part involves the short length scale followed by large length scale ordered structures. This phase diagram was calculated for values of (n, m) to the left of the bifurcation point in the classification diagram (figure 4.2). To the left of the bifurcation point there is gradual change from the short to the large length scale as a function of m. To the right of the bifurcation point a similar change from short to long length scale ordering will take place. However, on increasing m we also traverse through the region where the second order vertex function has two minima. On crossing the point where the minima are equal a discontinuous change in length scale occurs. Here, for some values of n and m the occurrence of complex stable structures which give rise to two minima should be expected, e.g. $c2mm$, $p2mm$, and $R\bar{3}m$.

Calculations in the framework of WSL, with two wave vectors belonging to the two different length scales, thus two amplitudes, led to *large* amplitudes thereby violating the assumption of WSL. Presumably, the higher harmonics of both length scales can not be ignored in the free energy expansion. This suggests that the WSL may not be applicable when two competing length scales are present (regions E, Ls and lS). This can of course be attributed to the fact that within this region one is not in the vicinity of a critical point. This indicates that when two competing length scales are present we should consider other theories, which do not suffer from the severe restrictions imposed by the weak segregation theory. The theory should e.g. be able to consider many harmonics or basis functions. A perfect candidate is the so-called self-consistent field theory [20] to be introduced in the next chapter.